

Domain switching in lead magnesium niobate-lead titanate polycrystalline sheets at single grain level

Wei-Sheng Su and Yang-Fang Chen

Department of Physics, National Taiwan University, Taipei 10617, Taiwan, Republic of China

Wan Y. Shih

School of Biomedical Engineering, Science, and Health Systems, Drexel University, Philadelphia, Pennsylvania 19104

Hongyu Luo and Wei-Heng Shih^{a)}

Department of Materials Science and Engineering, Drexel University, Philadelphia, Pennsylvania 19104

(Received 11 June 2007; accepted 9 August 2007; published online 11 September 2007)

The authors provide direct evidence of non-180° domain switching in the piezoelectric response of substrate-free 40 μm thick polycrystalline $[\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3]_{0.63}(\text{PbTiO}_3)_{0.37}$ (PMN-37PT) sheets under dc electric fields through piezoresponse force microscopy (PFM) at the single grain level. The sheet's polarization preferred pointing in the planar direction which was switched to the normal direction at electric field ranging between 1.3 and 1.9 kV/cm. An independent d_{31} measurement of PMN-37PT sheets deduced from the axial tip displacement measurements of a 4 mm long PMN-PT/copper cantilever showed enhanced d_{31} values that peaked at -2700 pm/V in the same range of electric field, consistent with the PFM observation. © 2007 American Institute of Physics.

[DOI: 10.1063/1.2778359]

Piezoelectric materials are important components in sensors and actuators. One major development in the piezoelectrics was the orientation-enhanced piezoelectric performance in a specially cut $\langle 010 \rangle$ lead magnesium niobate-lead titanate¹ (PMN-PT) solid solution and lead zinc niobate-lead titanate (PZN-PT) rhombohedral single crystals² that exhibit orientation-enhanced piezoelectric coefficients that are three times larger than those of their polycrystalline counterpart. More recently, we have observed sheet-geometry-enhanced piezoelectric response in polycrystalline sheets of lead magnesium niobate-lead titanate solid solution $[\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3]_{0.63}(\text{PbTiO}_3)_{0.37}$ (PMN-37PT) that was more than twice of that of $\langle 010 \rangle$ -cut PMN-PT single crystals and more than seven times that of the polycrystalline counterpart.³ *In situ* x-ray diffraction study showed that the PMN-37PT sheets retained a large portion of the tetragonal a domains and the rhombohedral domains even after their switching to the tetragonal c domains during poling. Furthermore, significant amount of the tetragonal a and the rhombohedral domains were switched to tetragonal c domains under an applied dc field. The observation of a large portion of the tetragonal a domains even after poling suggests that the depolarization effect in planar geometry^{4,5} occurs and that the reorientation of the in-plane polarization to the field direction causes a giant piezoelectric enhancement.

It is known that the piezoresponse force microscopy^{6,7} (PFM) can probe both the ferroelectric domain structures and the topographic features of an individual grain at the same time. In this letter, we will probe the polarization domain structures of a PMN-37PT freestanding sheet and its response to an applied dc electric field using PFM at the single grain level. Such direct polarization observations will yield critical information to understand the origin of the observed piezoelectric enhancement in the PMN-37PT sheets. Previ-

ously, the effect of ac electric field on piezoelectric films was studied by PFM,⁸ but no PFM study on the non-180° domain switching in ferroelectric films had been performed by varying dc field.

The PMN-37PT sheets were made first by dispersing crystalline lead magnesium niobate $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PMN) powders made from a colloidal coating approach^{9,10} in a lead titanate precursor solution containing lead acetate and titanium isopropoxide in ethylene glycol to yield a $\text{PMN}_{0.63}\text{-PT}_{0.37}$ (PMN-37PT) precursor powder with a nominal 10% lead excess. After drying at 300 °C, the PMN-37PT precursor powders were mixed with a proprietary dispersing resin and ball milled in an alcohol/ketone mixture for 24 h, followed by the addition of the remaining portion of the resin along with a phthalate-based plasticizer and ball milling for an additional 24 h. The slurry was then de-aired, casted into the desired thickness, and sintered in a doubly covered Al_2O_3 crucible at 1000 °C for 2 h.¹¹

PFM measurement was carried out using a modified scanning force microscope (Stand Alone SMENA apparatus, NT-MDT) with a platinum-iridium coated silicon tip (electrostatic force microscopy-PtIr5 coating, Nanoworld). Without an applied field, the PFM allowed topographic mapping of the sample surface. With an ac field applied between the PtIr-coated tip and the platinum bottom electrode on the back side of the PMN-37PT sheet, the PFM allowed for the recording of the vertical piezoelectric response (VPFM) and the lateral piezoelectric response (LPFM). The magnitude of the imaging ac field was chosen well below the coercive field of the PMN-37PT sheet and the frequency far above the low-pass cutoff of the force microscope feedback loop so as not to perturb the polarization configurations or the measurement circuit. With the imaging ac field, the normal and the in-plane components of the polarization gave rise to local vibrations in the thickness and the lateral directions, respectively, as a result of the converse piezoelectric effect, which were, respectively, monitored by cantilever bending (VPFM)

^{a)}Electronic mail: shiwh@drexel.edu

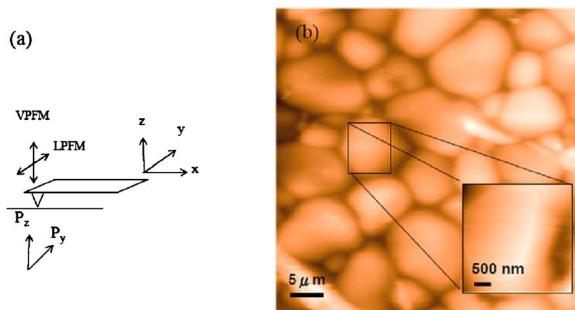


FIG. 1. (Color online) (a) Schematic of the PFM and the correlation of the VPFM with the vertical component of the polarization and that of the LPFM with the lateral component of the polarization a long the width direction of the PFM cantilever. (b) Atomic force microscopy image of the PMN-37PT freestanding film. The inset in Fig. 1(b) shows the region where the detailed PFM measurements were carried out.

and cantilever twisting or torsion (LPFM) using the lock-in techniques.¹² As depicted by the schematic in Fig. 1(a), the VPFM measures the z component of the polarization, P_z , and the LPFM the y component of polarization P_y assuming that the length of the PFM probe is pointing in the x direction.

A topographic image of a 40 μm thick PMN-37PT sheet is shown in Fig. 1(b). As can be seen, the grains of the PMN-37PT sheet were about 4 μm in size. For this study, the VPFM and LPFM were measured with an ac voltage of 1 V operated at 15 kHz. A dc bias field was also applied between the metal-coated cantilever tip and the bottom electrode to assess the effect of the dc field on the polarization domain patterns. Both the VPFM and the LPFM scan at a dc bias fields of 0, 1.3, and 1.9 kV/cm and back to a 0 kV/cm of the area shown in the inset of Fig. 1(b) are shown in Figs. 2(a)–2(h), respectively. In Figs. 2(a)–2(d), a bright (high VPFM) region represents a domain with a large P_z and a dark (small VPFM) region that of a small P_z and in Figs. 2(e)–2(h), a bright (high LPFM) region represents a domain of a large P_y and a dark (low LPFM) region that of a small P_y . As can be seen from Fig. 2(a), at 0 kV/cm, there were larger areas of dark regions than bright regions, indicating an overall low out-of-plane polarization. Note that the domain pattern shown in Fig. 2(e) was similar to that of Fig. 2(a), indicating that the polarization of the dark regions in both Figs. 2(a) and 2(e) was predominantly in the x direction and that of the bright region was predominantly in the y - z plane. Several other grains were studied and similar domain switching behaviors were observed. As the dc field increased to 1.3 and 1.9 kV/cm, the domain patterns disappeared. The VPFM became completely bright [see Figs. 2(b) and 2(c)] and the LPFM became mostly dark [see Figs. 2(f) and 2(g)], indicating that the polarization could be easily oriented by a dc bias field of 1.9 kV/cm. The observed domain switching behavior is consistent with the previous result that dc electric field could affect the dielectric and piezoelectric properties of thick PZT films via the non-180° domain switching.¹³ Xu *et al.*¹³ found that no non-180° domain switching could occur for fine grain-size PZT films of less than 2 μm thick. Here, we were able to see the non-180° domain switching effect because the pinning effect of the substrate was eliminated. This is the first time to show the dc-biased piezoelectric enhancement effect resulting from non-180° domains switching at the single grain level. When the field was reduced to 0 kV/cm [see Figs. 2(d) and 2(h)], dark regions returned and the domain pattern reappeared. This indicated that the field-

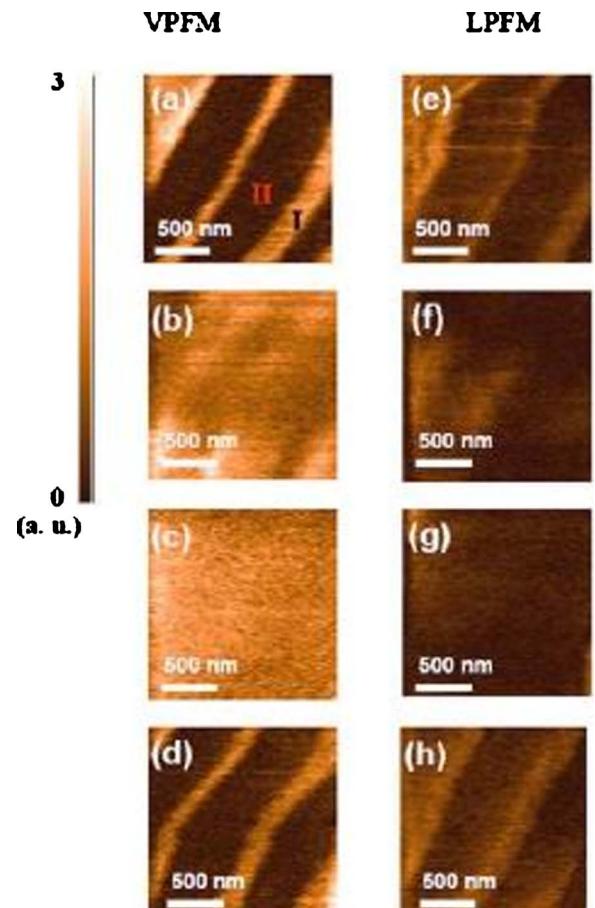


FIG. 2. (Color online) VPFM image of the inset of Fig. 1(b) at (a) 0 kV/cm (b) 1.3 kV/cm, (c) 1.9 kV/cm, and (d) back to 0 kV/cm and the LPFM of the same region at (e) 0, (f) 1.3, (g) 1.9, and (h) back to 0 kV/cm. The vertical scale bar indicates the intensity scale.

induced domain switching in this PMN-37PT sheet could be backswitched but not to the same configuration. The patterns in Figs. 2(a) and 2(d) are not the same because the path to the 0 kV/cm is different. Note that both Figs. 2(a) and 2(d) showed a larger area fraction of the dark regions at zero dc bias field, suggesting a preference for the domains to point in the lateral direction.

Although the domain patterns shown in Figs. 2(d) and 2(h) were not exactly the same as those shown in Figs. 2(a) and 2(e), it was remarkable that the polarization direction in the dark regions of Figs. 2(d) and 2(h) was mostly in the x direction, similar to that of the dark regions of Figs. 2(a) and 2(e). This indicates that there was a preferred polarization orientation at zero field, probably a result of the local fields generated by the neighboring grains.

As an example, the VPFM and LPFM of a spot in the bright region II and those of a spot in the dark region II were carried out at 0, 1.3, and 1.9 kV/cm. The resultant VPFM and LPFM versus the dc electric field are shown in Fig. 3(a), where the open squares and full squares represent the VPFM at regions I and at II, respectively, and open circles and full circles the LPFM at regions I and II, respectively. From Fig. 3(a), one can see that in region I (bright region), initially both the VPFM and LPFM were nonzero, indicating the polarization having the y and z components. In region II (the dark region), both the initial VPFM and the initial LPFM were small, indicating the polarization was mainly in the x direction. As the dc electric field was increased, the LPFM in

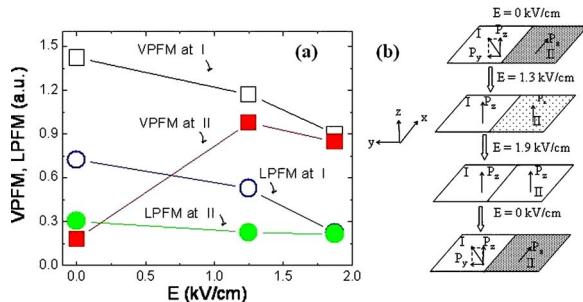


FIG. 3. (Color online) (a) VPFM and LPFM at region I and region II vs dc electric field. (b) Schematic of the polarization reorientation evolution with dc field. Note that the corresponding dc field is labeled on the top of (b).

both region I and region II diminished and the VPFM of the dark region increased to about the same level as that of the bright region, indicating that the lateral component of the polarization had been switched to the z direction in both regions. A schematic of the evolution of the polarization orientation in region I and region II that was consistent with the VPFM and LPFM evolutions of Fig. 3(a) is shown in Fig. 3(b). From these results, one can see that the polarization of the present PMN-37PT sheet can be completely switched to the normal direction at a dc electric field as low as 1.9 kV/cm at room temperature, a remarkable feature as compared to typical bulk polycrystalline samples and substrate-based films. Typical bulk polycrystalline samples required poling at fields larger than 10 kV/cm at temperatures close to the Curie temperature.^{14,15} On the other hand, typical switching fields of thin films were 50–300 kV/cm.^{13,16,17} One to two orders of magnitude reduction in switching field observed in the present freestanding sheets as compared to that of the substrate-based films may be attributed to the lack of substrate induced defects that normally pin the domain wall movement. The above results suggest that the large $-d_{31}$ values and the ease of domain switching observed in PMN-37PT sheets were a result of preferred orientation of in-plane polarization and the subsequent reorientation by the applied electric field. For direct comparison, in Fig. 4, we plot the $-d_{31}$ coefficient versus dc electric field of a 40 μm thick PMN-37PT sheet as deduced from the tip displacement measurement of a 4 mm long can-

tilever consisting of a 40 μm thick PMN-37PT layer and a 30 μm thick copper layer. The detail of the $-d_{31}$ deduction from the cantilever tip displacement can be found in Ref. 3. As can be seen from Fig. 4, the $-d_{31}$ of the 40 μm thick PMN-37PT sheet showed enhanced $-d_{31}$ which peaked at 2700 pm/V between 1.3 and 2 kV/cm coinciding with the PFM results. Although the geometry of PFM measurement (pointlike top electrode with platelike bottom electrode) is different from that of the cantilever of Fig. 4 (platelike top and bottom), the electric field in the PFM study may not be uniform. It was recently shown by Lin *et al.*¹⁷ that using the applied voltage divided by the thickness of the sample to calculate electric field in PFM is valid if a metal-coated tip is used. In fact, Lin *et al.*¹⁷ showed that the piezoresponse amplitude under the tip was constant over a range of about 1 μm , indicating a conductive tip that acts effectively like a top electrode of about micron size. With the highly conductive PtIr-coated tip used in our experiment, we expect the electric field in the sample to be reasonably uniform.

In summary, we have mapped out the polarization domain configuration and followed the polarization evolution at various dc electric fields using the PFM at the single grain level. The present 40 μm thick PMN-37PT sheet exhibited a preference for in-plane polarization at zero dc electric field. The in-plane polarization can be switched to the normal direction at a dc electric field ranging from 1.3 to 1.9 kV/cm. An independent $-d_{31}$ measurement of 40 μm thick PMN-37PT films as deduced from the axial tip displacement measurements of a 4 mm long PMN-PT/copper cantilever showed enhanced $-d_{31}$ values that peaked at 2700 pm/V between 1.3 and 2 kV/cm, consistent with the PFM observation.

This work was supported by Grant No. NSC94-2112-M-002-006 from the National Science Council of Republic of China and in part by the National Institute of Biomedical Imaging and Bioengineering (NIBIB), National Institute of Health (NIH) under Grant No. RO1EB00720-02. The authors thank Qing Zhu for electroding the samples.

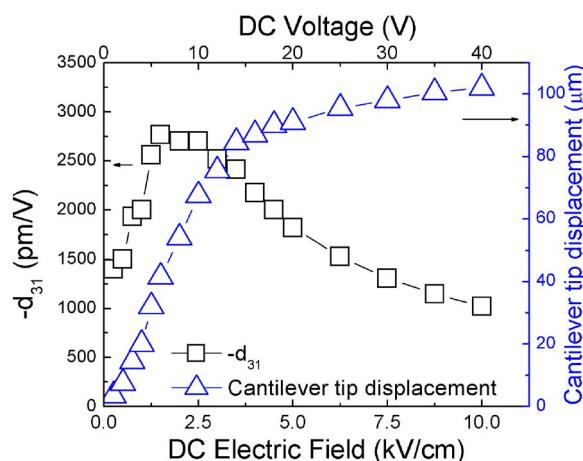


FIG. 4. (Color online) $-d_{31}$ vs dc electric field of 40 μm thick PMN-37PT freestanding films as deduced from the cantilever tip displacement measurement of a 4 mm long PMN-37PT/copper cantilever. Also shown is the tip displacement of the PMN-37PT/copper cantilever.

¹Data of commercially available products, APC International, Ltd.

²S.-E. Park and T. R. Shrout, *J. Appl. Phys.* **82**, 1804 (1997).

³W. Y. Shih, H. Luo, H. Li, C. Martorano, and W.-H. Shih, *Appl. Phys. Lett.* **89**, 242913 (2006).

⁴C. Kittel, *Introduction to Solid State Physics*, 5th ed. (Wiley, New York, 1976), Chap. 13, p. 404.

⁵W. Y. Shih, W.-H. Shih, and I. A. Aksay, *Phys. Rev. B* **50**, 15575 (1994).

⁶A. Roelofs, U. Bottger, R. Waser, F. Schlaphof, S. Trogisch, and L. M. Eng, *Appl. Phys. Lett.* **77**, 3444 (2000).

⁷B. J. Rodriguez, A. Gruverman, A. I. Kingon, R. J. Nemanich, and J. S. Cross, *J. Appl. Phys.* **95**, 1958 (2004).

⁸V. V. Shvartsman, N. A. Pertsev, J. M. Herrero, C. Zaldo, and A. L. Khoklin, *J. Appl. Phys.* **97**, 104105 (2005).

⁹H. Gu, W. Y. Shih, and W.-H. Shih, *J. Am. Ceram. Soc.* **86**, 217 (2003).

¹⁰H. Luo, W. Y. Shih, and W.-H. Shih, *Int. J. Appl. Ceram. Technol.* **1**, 146 (2004).

¹¹H. Luo, Ph.D. thesis, Drexel University, 2005.

¹²D. A. Scrymgeour and V. Gopalan, *Phys. Rev. B* **72**, 024103 (2005).

¹³F. Xu, S. Trolier-McKinstry, W. Ren, B. Xu, Z.-L. Xie, and K. J. Hemker, *J. Appl. Phys.* **89**, 1336 (2001).

¹⁴J. Kelly, M. Leonard, C. Tantigate, and A. Safari, *J. Am. Ceram. Soc.* **80**, 957 (1997).

¹⁵A. Bokov and Z.-G. Ye, *Phys. Rev. B* **66**, 094112 (2002).

¹⁶I.-D. Kim, Y. Avrahami, H. L. Tuller, Y.-B. Park, M. J. Dicken, and H. A. Atwater, *Appl. Phys. Lett.* **86**, 192907 (2005).

¹⁷H.-N. Lin, S.-H. Chen, S.-T. Ho, P.-R. Chen, and I.-N. Lin, *J. Vac. Sci. Technol. B* **21**, 916 (2003).